

**WHAT IS CLAIMED IS:**

- 5/2/81
1. A method of cleaning wafer surfaces, comprising the steps of:  
providing a wafer surface bearing overlying material thereon; and  
cleaning the wafer surface by removing at least a portion of the overlying material from the wafer surface by applying an aqueous solution comprising a major amount of one or more inorganic fluorine-comprising compounds and one or more organic acids in a ratio of about 100:1 to about 55:45, the solution having a pH of about 3 to about 9, such that the surface of the wafer is rendered substantially hydrophobic.
  2. The method of Claim 3, wherein the overlying material on the surface of the wafer comprises a low-k dielectric layer, and the step of cleaning the wafer surface comprises removing the dielectric layer at a rate of greater than about 1000 angstroms per minute.
  3. The method of Claim 2, wherein the aqueous solution comprises one or more hydrofluoric acid and one or more organic acids in a ratio of about 2:1 (v/v), such that the dielectric layer is removed at a rate of about 2500 angstroms per minute.
  4. The method of Claim 2, wherein the aqueous solution comprises at least ammonium fluoride and one or more organic acids in a ratio of about 2:1 (v/v).
  5. The method of Claim 1, wherein the overlying material on the surface of the wafer comprises a low-k dielectric layer, and the step of cleaning the wafer surface comprises removing the dielectric layer from the wafer surface at a rate of about 50 to about 1000 angstroms per minute.
  6. The method of Claim 5, wherein the aqueous solution comprises at least hydrofluoric acid and one or more organic acids in a ratio of about 1:2 (v/v), such that the dielectric layer is removed at a rate of about 400 to about 600 angstroms per minute.

7. The method of Claim 5, wherein the aqueous solution comprises at least ammonium fluoride and one or more organic acids in a ratio of about 2:1, such that the dielectric layer is removed at a rate of about 50-150 angstroms per minute.

8. The method of Claim 1, wherein the overlying material on the surface of the wafer comprises a low-k dielectric layer, and a photoresist layer overlying the dielectric layer and the step of cleaning the wafer surface comprises removing the dielectric layer and the photoresist layer at a rate of about 50 to about 1000 angstroms per minute.

9. The method of Claim 8, wherein the aqueous solution comprises at least hydrofluoric acid and one or more organic acids in a ratio of about 1:2 (v/v), such that the dielectric layer is removed at a rate of about 400 to about 600 angstroms per minute.

10. The method of Claim 9, wherein the aqueous solution comprises at least ammonium fluoride and one or more organic acids in a ratio of about 2:1 (v/v), such that the dielectric layer is removed at a rate of about 100 angstroms per minute.

11. The method of Claim 1, wherein the composition is an aqueous solution consisting essentially of the one or more inorganic fluorine-comprising compounds and the one or more organic acids.

12. A method for surface treating wafer surfaces, comprising the steps of:  
providing a wafer surface having a low-k dielectric layer disposed thereon and a photoresist layer overlying the dielectric layer; and  
treating the wafer surface to remove at least a portion of the dielectric layer with minimal removal of the photoresist layer, by applying an aqueous solution of one or more inorganic fluorine-comprising compounds and one or more organic acids, the solution having a pH of about 3 to about 9, such that the dielectric layer is removed selective to the photoresist at a rate of greater than about 1000 angstroms per minute.

13. The method of Claim 12, wherein the aqueous solution comprises at least hydrofluoric acid and the one or more organic acids in a ratio of about 2:1 (v/v), such that the dielectric layer is selectively removed at a rate of about 2300 to about 2700 angstroms per minute.

14. The method of Claim 12, wherein the aqueous solution comprises at least ammonium fluoride and the one or more organic acids in a ratio of about 2:1 (v/v).

15. A method for surface treating wafer surfaces, comprising the steps of:

providing a wafer surface having a low-k dielectric layer disposed thereon and a photoresist layer overlying the dielectric layer; and

treating the wafer surface to remove at least a portion of the dielectric layer with minimal removal of the photoresist layer, by applying an aqueous solution of one or more inorganic fluorine-comprising compounds and one or more organic acids in a ratio of about 1:2 (v/v), and having a pH of about 3 to about 9 such that the dielectric layer is removed selective to the photoresist at a rate of about 50 to about 1000 angstroms per minute.

16. The method of Claim 15, wherein the aqueous solution comprises at least hydrofluoric acid, and the dielectric layer is selectively removed at a rate of about 400 to about 600 angstroms per minute.

17. The method of Claim 15, wherein the aqueous solution comprises at least ammonium fluoride and the one or more organic acids in a ratio of about 2:1 (v/v), such that the dielectric layer is selectively removed at a rate of about 50 to about 150 angstroms per minute.

18. A post-etch cleaning to selectively remove a low-k dielectric material from a wafer, comprising:

providing a wafer surface having a layer of the low-k dielectric material disposed thereon and a photoresist layer overlying the dielectric layer; and

treating the wafer surface to remove at least a portion of the dielectric layer, by apply an aqueous solution of a least one inorganic fluorine-comprising compound and at least one organic acid component in a ratio of about 1:2 (v/v), the solution having a pH of about 3 to about 9, such that the removal rate of the low-k dielectric material is controlled at about 50 to about 1000 angstroms per minute.

19. A method of cleaning wafer surfaces, the method comprising the steps of:

providing an aqueous solution comprising at least one inorganic fluorine-comprising compound and at least one organic acid;

providing a wafer having an unmasked low-k dielectric material disposed on at least a portion of one surface; and

contacting the surface of the wafer having the low-k dielectric material thereon with the aqueous solution under conditions effective to remove at least a portion of the low-k dielectric material at a rate of greater than about 1000 angstroms per minute.

5/23 20. A method of cleaning wafer surfaces, the method comprising the steps of:

providing an aqueous solution comprising at least one inorganic fluorine-comprising compound selected from the group consisting of hydrofluoric acid and ammonium fluoride, and mixtures thereof; and at least one organic acid selected from the group consisting of citric acid, acetic acid, ascorbic acid, and mixtures thereof;

providing a wafer having a low-k dielectric material disposed on at least a portion of one surface; and

contacting the surface of the wafer having the low-k dielectric material thereon with the aqueous solution under conditions effective to remove at least a portion of the low-k dielectric material at a rate of about 50 to about 1000 angstroms per minute.

21. The method of Claim 20, wherein the aqueous solution comprises about 30 % to about 70 % by volume of the fluorine-comprising compound, and about 30 % to about 70 % by volume of the organic acid, based on the total volume of the solution.

22. The method of Claim 20, wherein the aqueous solution includes at least hydrofluoric acid and at least one organic acid in a ratio of about 1:2 (v/v), to remove at least a portion of the low-k material at a rate of about 400 to about 600 angstroms per minute.

23. The method of Claim 22, wherein the aqueous solution includes about 30 to about 40 % by volume of hydrofluoric acid, and about 60 to about 70 % by volume of the organic acid.

24. The method of Claim 20, wherein the aqueous solution includes at least ammonium fluoride and at least one organic acid in a ratio of about 2:1 (v/v), to remove at least a portion of the low-k material at a rate of about 50 to about 150 angstroms per minute.

25. The method of Claim 24, wherein the aqueous solution includes about 60 to about 70 % by volume of ammonium fluoride, and about 30 to about 40 % by volume of the organic acid.

26. A method of cleaning wafer surfaces, the method comprising the steps of:  
providing an aqueous solution comprising an inorganic fluorine-comprising compound selected from the group consisting of hydrofluoric acid and ammonium fluoride, and mixtures thereof; and an organic acid selected from the group consisting of citric acid, acetic acid, ascorbic acid, and mixtures thereof;  
providing a wafer having a low-k dielectric material disposed on at least a portion of one surface; and  
contacting the surface of the wafer having the low-k dielectric material thereon with the aqueous solution under conditions effective to remove at least a portion of the low-k dielectric material at a rate greater than about 1000 angstroms per minute.

27. The method of Claim 26, wherein the aqueous solution includes at least hydrofluoric acid and one or more organic acids in a ratio of about 2:1 (v/v).

28. The method of Claim 27, wherein the aqueous solution includes about 63 to about 70 % by volume of hydrofluoric acid, and about 30 to about 36 % by volume of the one or more organic acids.

29. The method of Claim 26, wherein the aqueous solution includes at least ammonium fluoride and one or more organic acids in a ratio of about 2:1 (v/v).

30. The method of Claim 26, wherein the aqueous solution includes about 63 to about 70 % by volume of ammonium fluoride, and about 30 to about 36 % by volume of the one or more organic acids.

31. A method of surface treating wafer surfaces, comprising the steps of:  
providing a wafer surface having a low-k dielectric layer disposed thereon and a photoresist layer overlying the dielectric layer; and  
providing an aqueous composition comprising at least one inorganic fluorine-comprising compound, and a major amount of one or more organic acids; and  
contacting the surface of the wafer having the low-k dielectric and photoresist layers thereon with the composition under conditions effective to selectively remove the photoresist layer while leaving the low-k layer essentially intact on the substrate.

32. The method of Claim 31, wherein the composition comprises an aqueous solution of at least hydrofluoric acid and the one or more organic acids in a ratio of about 1:100 to about 45:55 (v/v), such that the composition removes the photoresist mask completely from the surface selective to the dielectric layer

33. The method of Claim 31, wherein the inorganic fluorine-comprising compound is selected from the group consisting of hydrofluoric acid, ammonium fluoride, and mixtures thereof; and the organic acid is selected from the group consisting of citric acid, gallic acid, acetic acid, formic acid, propionic acid, n-butyric acid, isobutyric acid, benzoic acid, ascorbic

acid, gluconic acid, malic acid, malonic acid, oxalic acid, succinic acid, tartaric acid, and mixtures thereof.

34. The method of Claim 31, wherein the organic acid is selected from the group consisting of citric acid, acetic acid, ascorbic acid, and mixtures thereof.

35. The method of Claim 31, wherein the step of contacting the surface of the wafer comprises immersing the wafer in a bath of the composition, spraying the surface of the wafer with the composition, exposing the wafer to a vapor, or any combination thereof.

36. A method of cleaning wafer surfaces, comprising:

formulating an aqueous composition for selectively removing at least a portion of a low-k dielectric layer from a wafer surface at a predetermined rate, the composition consisting essentially of one or more inorganic fluorine-comprising compounds and one or more organic acids, and having a pH of about 3 to about 9;

providing a wafer having a low-k dielectric material disposed on at least a portion of one surface; and

contacting the wafer having the low-k dielectric material thereon with the composition under conditions effective to remove at least a portion of the low-k dielectric material at the predetermined rate.

37. The method of Claim 36, wherein the inorganic fluorine-comprising compound is selected from the group consisting of hydrofluoric acid, ammonium fluoride, and mixtures thereof; and the organic acid is selected from the group consisting of citric acid, acetic acid, ascorbic acid, and mixtures thereof.

38. The method of Claim 36, wherein the composition is formulated to remove the dielectric layer at a rate greater than about 1000 angstroms per minute.

39. The method of Claim 36, wherein the composition is formulated to remove the dielectric layer at a rate of about 50 to about 1000 angstroms per minute.

40. The method of Claim 36, wherein at least a portion of the low-k dielectric layer is unmasked.

41. The method of Claim 36, wherein at least a portion of the low-k dielectric layer is masked by an overlying layer of photoresist.

42. The method of Claim 41, wherein the composition is formulated to remove the dielectric layer and the photoresist layer from the surface of the wafer, such that the surface of the substrate is rendered substantially hydrophobic.

43. The method of Claim 41, wherein the composition is formulated to remove the dielectric layer selective to the photoresist at a rate of about 50 to about 1000 angstroms per minute.

44. The method of Claim 41, wherein the composition is formulated to remove the dielectric layer selective to the photoresist at a rate of greater than about 1000 angstroms per minute.

45. A method of cleaning wafer surfaces, comprising:

formulating an aqueous composition for selectively removing at least a portion of a low-k dielectric layer disposed on the wafer surface at a predetermined rate, the composition consisting essentially of one or more organic fluorine-comprising compounds and one or more inorganic acids, and having a pH of about 3 to about 9;

providing a wafer having a low-k dielectric material disposed on at least a portion of one surface; and

contacting the wafer having the low-k dielectric material thereon with the composition under conditions effective to remove at least a portion of the low-k dielectric material at the predetermined rate.



46. The method of Claim 45, wherein the organic fluorine-comprising compound is selected from the group consisting of hydrogen fluoride pyridinium, triethylamine trihydrofluoride, tetramethylammonium fluoride, and mixtures thereof.

47. The method of Claim 45, wherein the inorganic acid is selected from the group consisting of sulfuric acid, nitric acid, hydrochloric acid, phosphoric acid, and mixtures thereof.

48. The method of Claim 45, wherein the composition is formulated to remove the dielectric layer at a rate greater than about 1000 angstroms per minute.

49. The method of Claim 45, wherein the composition is formulated to remove the dielectric layer at a rate of about 50 to about 1000 angstroms per minute.

50. The method of Claim 45, wherein at least a portion of the low-k dielectric layer is unmasked.

51. The method of Claim 45, wherein at least a portion of the low-k dielectric material is masked by an overlying layer of photoresist.

52. The method of Claim 51, wherein the composition is formulated to remove the dielectric layer and the photoresist layer from the surface of the wafer such that the surface of the substrate is rendered substantially hydrophobic.

53. The method of Claim 51, wherein the composition is formulated to remove the dielectric layer selective to the photoresist at a rate of about 50 to about 1000 angstroms per minute.

54. The method of Claim 51, wherein the composition is formulated to remove the dielectric layer selective to the photoresist at a rate of greater than about 1000 angstroms per minute.

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54. A composition for cleaning or treating a surface of a semiconductor wafer, comprising: an aqueous solution of a major amount of one or more inorganic fluorine-comprising compounds and one or more organic acids in a ratio of about 100:1 to about 55:45 (v/v), to remove organic material and low-k dielectric material from the surface of the wafer whereby the surface of the substrate is rendered substantially hydrophobic; the composition having a pH of about 3 to about 9.

56 55  
55. The composition of Claim 54, wherein the inorganic fluorine-comprising compound is selected from the group consisting of hydrofluoric acid, ammonium fluoride, and mixtures thereof.

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56. The composition of Claim 54, wherein the organic acid is selected from the group consisting of citric acid, gallic acid, acetic acid, formic acid, propionic acid, n-butyric acid, isobutyric acid, benzoic acid, ascorbic acid, gluconic acid, malic acid, malonic acid, oxalic acid, succinic acid, tartaric acid, and mixtures thereof.

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57. The composition of Claim 54, wherein the organic acid is selected from the group consisting of citric acid, acetic acid, ascorbic acid, and mixtures thereof.

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58. The composition of Claim 54, wherein the aqueous solution consists essentially of the one or more inorganic fluorine-comprising compounds and the one or more organic acids.

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59. The composition of Claim 54, wherein the aqueous solution includes at least hydrofluoric acid and at least one organic acid in a ratio of about 1:2 (v/v).

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60. The composition of Claim 59, wherein the aqueous solution includes about 30 to about 40 % by volume of hydrofluoric acid, and about 60 to about 70 % by volume of the organic acid.

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61. The composition of Claim 54, wherein the aqueous solution includes at least ammonium fluoride and at least one organic acid in a ratio of about 2:1 (v/v).

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62. The composition of Claim 61, wherein the aqueous solution includes about 60 to about 70 % by volume of ammonium fluoride, and about 30 to 40 % by volume of the organic acid.

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63. A composition for cleaning or treating a surface of a semiconductor wafer, comprising:  
an aqueous solution of a major amount of one or more organic fluorine-comprising compounds and one or more inorganic acids in a ratio of about 1:5 (v/v), to remove organic material and low-k dielectric material from the surface of the wafer such that the surface of the substrate is rendered substantially hydrophobic; the composition having a pH of about 3 to about 9.

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64. The composition of Claim 63, wherein the organic fluorine-comprising compound is selected from the group consisting of hydrogen fluoride pyridinium, tetramethylammonium fluoride, triethylamine trihydrofluoride, and mixtures thereof.

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65. The composition of Claim 63, wherein the inorganic acid is selected from the group consisting of sulfuric acid, nitric acid, hydrochloric acid, phosphoric acid, and mixtures thereof.

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66. The composition of Claim 63, wherein the aqueous solution consists essentially of the one or more organic fluorine-comprising compounds and the one or more inorganic acids.

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67. A composition for surface treating wafer surfaces, comprising:  
an aqueous solution of a major amount of one or more inorganic fluorine-comprising compounds and one or more organic acids to remove organic material and low-k dielectric material from the surface of the wafer, such that the dielectric layer is removed selective to the photoresist at a rate of about 50 to about 1000 angstroms per minute; the composition having a pH of about 3 to about 9.

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68. The composition of Claim 67, wherein the aqueous solution comprises at least hydrofluoric acid, and the dielectric layer is selectively removed at a rate of about 400 to about 600 angstroms per minute.

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69. The composition of Claim 67, wherein the aqueous solution comprises at least ammonium fluoride and the one or more organic acids in a ratio of about 2:1 (v/v), such that the dielectric layer is selectively removed at a rate of about 50 to about 150 angstroms per minute.

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70. The composition of Claim 67, wherein the composition is an aqueous solution consisting essentially of the one or more inorganic fluorine-comprising compounds and the one or more organic acids.

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71. A composition for surface treating wafer surfaces, comprising:  
an aqueous solution of a major amount of one or more inorganic fluorine-comprising compounds and one or more organic acids to remove organic material and low-k dielectric material from the surface of the wafer, such that the dielectric layer is removed selective to the photoresist at a rate up to than about 1000 angstroms per minute; the composition having a pH of about 3 to about 9.

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72. The composition of Claim 71, wherein the aqueous solution comprises at least hydrofluoric acid and the one or more organic acids in a ratio of about 1:2 (v/v), whereby the dielectric layer is selectively removed at a rate of about 400 to about 600 angstroms per minute.

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73. The composition of Claim 71, wherein the aqueous solution comprises at least ammonium fluoride and the one or more organic acids in a ratio of about 2:1 (v/v), whereby the dielectric layer is selectively removed at a rate of about 50 to about 150 angstroms per minute.

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